Bath generated work extraction and inversion-free gain in two-level systems

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The spin-boson model, often used in NMR and ESR physics, quantum optics and spintronics, is considered in a solvable limit to model a spin one-half particle interacting with a bosonic thermal bath. By applying external pulses to a non-equilibrium initial state of the spin, work can be extracted from the thermalized bath. It occurs on the timescale $\mathcal{T}_2$ inherent to transversal ('quantum') fluctuations. The work (partly) arises from heat given off by the surrounding bath, while the spin entropy remains constant during a pulse. This presents a violation of the Clausius inequality and the Thomson formulation of the second law (cycles cost work) for the two-level system.

Starting from a fully disordered state, coherence can be induced by employing the bath. Due to this, a gain from a positive-temperature (inversion-free) two-level system is shown to be possible.

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After E.L. Hahn discovered the spin-echo in NMR physics [1], it was soon suspected to violate the second law [1,2]; for a recent discussion discussion see e.g. [2,3]. As a precursor to this question, we shall investigate in this Letter whether single or double pulses on single spins coupled to a bath already mark a violation of this law.

Recently we analyzed the thermodynamics of the Caldeira-Leggett model for a quantum harmonic oscillator coupled to a quantum harmonic bath [4,5]. At low temperatures various formulations of the second law are violated: the Clausius inequality $đ\mathcal{Q} \leq T\mathrm{d}S$ is broken, the rates of energy dispersion and entropy production can be negative, and certain cycles are possible where heat extracted from the bath is fully converted into work ("perpetuum mobile"). These findings are nevertheless in agreement with the Thomson formulation of the second law (cycles cost work) applied to an equilibrium initial distribution, for which an exact proof exists [6].

The cause of the breakdown the universal thermodynamic picture is the occurrence of a cloud of interaction modes (photons or phonons) around the central system. Such a cloud is already familiar from the dressed electron picture in quantum electrodynamics. For systems of our interest, the cloud is not present at high temperatures, but, due to the non-vanishing coupling to the bath, it builds up at low T, inducing non-thermodynamic physics.

Two level systems [7,8], like electrons or two-state atoms in a field, or a two level Josephson junction, display relaxational behavior due to coupling to a bath. Transversal and longitudinal correlations relax on timescales $\mathcal{T}_2$ and $\mathcal{T}_1$, respectively, with typically $\mathcal{T}_2 \ll \mathcal{T}_1$ [8], since energy transfer is not involved in the $\mathcal{T}_2$- process.

The Hamiltonian of the problem reads:

$$\mathcal{H} = \mathcal{H}_S + \mathcal{H}_B + \mathcal{H}_I, \quad \mathcal{H}_S = \frac{\varepsilon}{2}\hat{\sigma}_z + \frac{\Delta}{2}\hat{\sigma}_x, \tag{1}$$

$$\mathcal{H}_B = \sum_k \hbar\omega_k \hat{a}_k^\dagger \hat{a}_k, \quad \mathcal{H}_I = \frac{1}{2}\sum_k g_k(\hat{a}_k^\dagger + \hat{a}_k)\hat{\sigma}_z.$$

This is a spin $\frac{1}{2}$ interacting with a bath of harmonic oscillators (spin-boson model [7,9]); $\mathcal{H}_S$, $\mathcal{H}_B$ and $\mathcal{H}_I$ stand for the Hamiltonians of the spin, the bath and their interaction, respectively. $\hat{\sigma}_x$, $\hat{\sigma}_y$ and $\hat{\sigma}_z = -i\hat{\sigma}_x\hat{\sigma}_y$ are Pauli matrices, and $\hat{a}_k^\dagger$ and $\hat{a}_k$ are the creation and annihilation operators of the bath oscillator with the index k, while the g_k are the coupling constants. For an electron in a magnetic field B, $\varepsilon = \bar{g}\mu_B B$ is the energy, with $\bar{g}$ the gyro-magnetic factor and μ_B the Bohr magneton. We shall restrict ourselves to the model with $\Delta = 0$, which is a prototype of a variety of physical systems [7], and known to be exactly solvable [7,9], since z-component of the spin is conserved, and with it the spin energy. Physically it means that we restrict ourselves to times much less than $\mathcal{T}_1$. In NMR (ESR) physics [8] the model represents a spin (electron) interacting with a bath of phonons. In quantum optics it is suitable for describing a two-level atom interacting with a photonic bath.

Starting from general physical arguments [7], one typically takes the quasi-Ohmic spectral density of the bath

$$J(\omega) = \sum_k \frac{g_k^2}{\hbar\omega_k}\delta(\omega_k - \omega) = \frac{g\hbar}{\pi}e^{-\omega/\Gamma}, \tag{2}$$

where g is the dimensionless damping constant and the exponential cuts off the coupling at $\omega \gg \Gamma$, the maximal frequency of the bath. As usual, the thermodynamic limit for the bath has been taken here.

Since $\Delta = 0$, one has conservation of $\hat{\sigma}_z(t) = \hat{\sigma}_z(0)$ (in the Heisenberg picture). The dynamics of the annihilation operator of the k'th bath mode reads

$$\hat{a}_k(t) = e^{-i\omega_k t}\hat{a}_k(0) + \frac{g_k\hat{\sigma}_z}{2\hbar\omega_k}\left(e^{-i\omega_k t} - 1\right). \tag{3}$$

This implies

$$\sum_k g_k[\,\hat a_k^\dagger(t)+\hat a_k(t)\,]=\hat\eta(t)-\hat\sigma_z\,G(t), \tag{4}$$

where we denoted the quantum noise operator

$$\hat\eta(t)=\sum_k g_k[\hat a_k^\dagger(0)e^{i\omega_k t}+\hat a_k(0)e^{-i\omega_k t}], \tag{5}$$

which will act as a random force on the spin, and where

$$G(t)=\sum_k\frac{g_k^2}{\hbar\omega_k}(1-\cos\omega_k t)=g\frac{\hbar\Gamma}{\pi}\frac{\Gamma^2t^2}{1+\Gamma^2t^2}, \tag{6}$$

showing that $1/\Gamma$ is the relaxation time of the bath.

Separated initial state. To describe situations, where the spin was suddenly brought into the contact with the bath, e.g. an electron injected into semiconductor, atom injected into a cavity, or exciton created by external radiation, we make the assumption that initially, at $t=0$, the spin and the bath are in a separated state, the latter being Gibbsian at temperature $T=1/\beta$: $\rho(0)=\rho_S(0)\otimes\exp(-\beta\mathcal{H}_B)/Z_B$, where $\rho_S(0)$ is the initial density matrix of the spin. In this situation the quantum noise is stationary and Gaussian with average zero and time-ordered autocorrelation function: $K_{\mathcal T}(t-t')=\langle\mathcal{T}[\hat\eta(t)\hat\eta(t')]\rangle$, where $\mathcal T$ stands for the time-ordering operator and the brackets for the trace over the initial state. For $t>0$ it holds that

$$K_{\mathcal T}(t)=K(t)-i\,\hbar\dot G(t)\equiv\hbar^2[\ddot\xi(t)-i\,\ddot G_1(t)] \tag{7}$$

where an explicit calculation yields

$$\xi(t)=\frac{g}{\pi}\,\ln\frac{\Gamma^2\left(1+\frac{T}{\hbar\Gamma}\right)\,\sqrt{1+\Gamma^2t^2}}{\Gamma\left(1+\frac{T}{\hbar\Gamma}-i\frac{Tt}{\hbar}\right)\Gamma\left(1+\frac{T}{\hbar\Gamma}+i\frac{Tt}{\hbar}\right)} \tag{8}$$

$$G_1(t)=\frac{g}{\pi}\Gamma t-\gamma(t),\qquad \gamma(t)=\frac{g}{\pi}\arctan\Gamma t \tag{9}$$

The spin operators $\hat\sigma_\pm=\hat\sigma_x\pm i\,\hat\sigma_y$ satisfy

$$\dot{\hat\sigma}_\pm=\frac{i}{\hbar}\,\left[\,\pm\varepsilon+\hat\eta(t)-G(t)\,\right]\,\hat\sigma_\pm \tag{10}$$

and have, with $\omega_0=\varepsilon/\hbar$, the solution

$$\hat\sigma_\pm(t)=\exp\left(\pm\,i\omega_0 t\ \right)\,\hat\Pi_\pm(t,0)\,\hat\sigma_\pm(0) \tag{11}$$

$$\hat\Pi_\pm(t_1,t_0)\equiv e^{-i\,G_1(t_1-t_0)}\,\mathcal{T}\,\exp\left[\pm\frac{i}{\hbar}\int_{t_0}^{t_1}\mathrm{d}s\,\hat\eta(s)\right], \tag{12}$$

Depending only on $a_k(0)$ and $a_k^\dagger(0)$, it commutes with $\hat\sigma_{x,y,x}(0)$. Thus one gets

$$\langle\hat\sigma_+(t)\rangle=\exp\left(i\omega_0 t\,\right)\,\left\langle\,\hat\Pi_+(t,0)\,\right\rangle\langle\hat\sigma_+(0)\rangle, \tag{13}$$

Evaluating the time ordered product term-by-term with help of Wick's theorem and resumming, we obtain

$$\left\langle\,\hat\Pi_+(t_1,t_0)\,\right\rangle=\exp[-\xi(t_1-t_0)], \tag{14}$$

The result is stationary, as it should. Substituting (14) into (13), the and real and imaginary parts give

$$\langle\hat\sigma_x(t)\rangle=[\cos\omega_0 t\,\langle\hat\sigma_x(0)\rangle-\sin\omega_0 t\,\langle\hat\sigma_y(0)\rangle]\ e^{-\xi(t)} \tag{15}$$

$$\langle\hat\sigma_y(t)\rangle=[\sin\omega_0 t\,\langle\hat\sigma_x(0)\rangle+\cos\omega_0 t\,\langle\hat\sigma_y(0)\rangle]\ e^{-\xi(t)} \tag{16}$$

For $t\gg 1/\Gamma$ Eq. (8) brings

$$\xi(t)\approx\frac{t}{\mathcal{T}_2},\qquad \mathcal{T}_2=\frac{1}{g}\,\frac{\hbar}{T} \tag{17}$$

$\mathcal{T}_2$ can thus be identified with the transversal decay time. For small g this is a strong enhancement of the quantum-timescale $\hbar/T$. The most optimistic case, $\mathcal{T}_2\sim 100$ s at room temperature, involves $g\sim10^{-16}$, truly small.

The density matrix of the spin reads

$$\rho_S=\frac12\left[\,1+\langle\hat\sigma_x(t)\rangle\,\hat\sigma_x+\langle\hat\sigma_y(t)\rangle\,\hat\sigma_y+\langle\hat\sigma_z(t)\rangle\,\hat\sigma_z\,\right]. \tag{18}$$

Its von Neumann entropy equals $S_{\rm vN}=-{\rm tr}\rho_S\ln\rho_S=-p_1\ln p_1-p_2\ln p_2$, where $p_{1,2}=\frac12\pm\frac12|\langle\vec\sigma\rangle|$. In the course of time $|\langle\vec\sigma(t)\rangle|$ decays to $|\langle\hat\sigma_z(0)\rangle|$, which makes the von Neumann entropy increase. Since there is no heat flow - the energy is conserved - this is in agreement with a formulation of the second law: the entropy of closed system, or of an open system without energy transfer (the spin in contact with the bath), cannot decrease.

A sudden pulse. We mostly consider the Hamiltonian (1) with $\Delta=0$. A fast rotation around the x-axis is described by taking $\Delta\neq0$ during a short time δ_1; this is called a fast pulse [8]. If $\Delta\sim1/\delta_1$ is large, the evolution operator describing the pulse becomes $U_1=\exp(-i\delta_1\mathcal{H}(\Delta)/\hbar)\approx\exp(\frac12 i\,\theta\hat\sigma_x)+\mathcal{O}(\delta_1)$, where $\theta=-\delta_1\Delta/\hbar$ is the rotation angle,

$$U_1^{-1}\,\hat\sigma_y\,U_1=\hat\sigma_z\sin\theta+\hat\sigma_y\cos\theta, \tag{19}$$

$$U_1^{-1}\,\hat\sigma_z\,U_1=\hat\sigma_z\cos\theta-\hat\sigma_y\sin\theta. \tag{20}$$

When suddenly switching Δ on and off, the state of the system does not change, so $\rho(t+\delta_1)=U_1\,\rho(t)\,U_1^{-1}$. The work done by the source is the change of the total energy which reads, since $[U_1,\mathcal{H}(\Delta)]=0$,

$$\begin{aligned}W_1(t)&={\rm tr}\left[\rho(t)(\mathcal{H}(\Delta)-\mathcal{H})+\rho(t+\delta_1)(\mathcal{H}-\mathcal{H}(\Delta))\right]\\&={\rm tr}\,\rho(t)(U_1^{-1}\mathcal{H}U_1-\mathcal{H}),\end{aligned} \tag{21}$$

The work done in this variation appears to be

$$\begin{aligned}W_1=&\ -\frac{\varepsilon}{2}\,(1-\,\cos\theta\,)\langle\hat\sigma_z(0)\rangle-\frac{\varepsilon}{2}\sin\theta\,\langle\hat\sigma_y(t)\rangle\\&+\frac12(1-\,\cos\theta\,)\,G(t)-\frac{\hbar\dot\xi(t)}{2}\sin\theta\,\langle\hat\sigma_x(t)\rangle\end{aligned} \tag{22}$$

Our main interest is work extraction from the bath. In order to ensure that the pulse does not change the energy of the spin, we first consider the case $\varepsilon=0$, where the

spin has no energy. For small g, $\theta=-\pi/2$ and $t\gg 1/\Gamma$ one gets

$$W_1=\frac{g\hbar\Gamma}{2\pi}+\frac{gT}{2}\langle\hat\sigma_x(0)\rangle\, e^{-t/\mathcal{T}_2} \tag{23}$$

If for a fixed t, temperature is neither too large nor too small, $Te^{-t/\mathcal{T}_2}>\hbar\Gamma/\pi$, work can be extracted ($W_1<0$), provided the spin started in a coherent state $\langle\hat\sigma_x(0)\rangle=-1$. This possibility to *extract work from the bath* disappears on the timescale $\mathcal{T}_2$, because then the spin looses its coherence, $\langle\hat\sigma_{x,y}(t)\rangle\to 0$. Without a pulse the spin energy is conserved, however. Notice that any combination of $\pm\pi$ pulses (this is a classical variation, since the coherence is not involved) can extract work only from a non-thermalized bath, i.e. for times $\sim 1/\Gamma$.

Initial preparation via a rotation. Our approach also allows to consider a specific, well controllable non-equilibrium initial state: a Gibbsian of the total system, $\rho_G=\exp(-\beta\mathcal{H})/Z$, in which at $t=0$ the spin is rotated over an angle $-\frac{1}{2}\pi$ around the y-axis, $\rho(0)=U_0\,\rho_G\,U_0^{-1}$, with $U_0=\exp(-i\pi\hat\sigma_y/4)$. This maps $\hat\sigma_x\to\hat\sigma_z$, $\hat\sigma_z\to -\hat\sigma_x$. Such a state models the optical excitation of the spin, as it is done in NMR and spintronics. Though $\rho(0)$ does not have the product form, the problem remains exactly solvable. Taking $\theta=-\frac{1}{2}\pi$ one now gets

$$\begin{aligned}W_1&=\frac{G(t)}{2}-\Big[\frac{\varepsilon}{2}(\sin\omega_0 t\,\cos\gamma\tanh\frac{\beta\varepsilon}{2}+\cos\omega_0 t\,\sin\gamma)\\&+\frac{\dot\xi(t)}{2}(\cos\omega_0 t\,\cos\gamma\tanh\frac{\beta\varepsilon}{2}-\sin\omega_0 t\,\sin\gamma)\Big]\,e^{-\xi(t)}\\&\approx\frac{g\hbar\Gamma}{2\pi}-\Big[\frac{\varepsilon}{2}\sin\omega_0 t+\frac{gT}{2}\cos\omega_0 t\Big]\tanh\frac{\beta\varepsilon}{2}\;e^{-t/\mathcal{T}_2}\end{aligned} \tag{24}$$

where $\gamma(t)$ of Eq. (9) arises from friction, with $\gamma(\infty)=\frac{1}{2}g$, and where $\omega_0=\varepsilon/\hbar$. Typically g is small, so work is extracted ($W_1<0$) when the sinus is positive. The work decomposes,

$$W_1=\Delta U-\Delta Q \tag{25}$$

into the change in spin energy due to the pulse,

$$\begin{aligned}\Delta U&=\frac{\varepsilon}{2}[\langle\hat\sigma_z(t^+)\rangle-\langle\hat\sigma_z(t^-)\rangle]=\frac{\varepsilon}{2}\langle\hat\sigma_x(t^-)\rangle\\&=-\frac{\varepsilon}{2}[\sin\omega_0 t\,\cos\gamma\tanh\frac{\beta\varepsilon}{2}+\cos\omega_0 t\,\sin\gamma]\,e^{-\xi(t)}\\&\approx-\frac{\varepsilon}{2}\sin\omega_0 t\,\tanh\frac{\beta\varepsilon}{2}\,e^{-t/\mathcal{T}_2},\end{aligned} \tag{26}$$

and the heat absorbed from the bath

$$\Delta Q\approx\frac{g}{2}\left[-\frac{\hbar\Gamma}{\pi}+T\cos\omega_0 t\;\tanh\frac{\beta\varepsilon}{2}\,e^{-t/\mathcal{T}_2}\right] \tag{27}$$

Notice its similarity with $-W_1$ of Eq. (23). An interesting case is where work is performed by the total system ($W_1<0$) solely due to heat taken from the bath ($\Delta Q>0$, $\Delta U=0$). This process, possible by choosing $t\approx 2\pi n/\omega_0$ with integer n, can be considered as a cycle of a perpetuum mobile, forbidden by folklore minded formulations of the second law. Indeed, under a rotation the length $|\langle\vec\sigma\rangle|$, and with it the von Neumann entropy, is left invariant, so one has a process with $\Delta Q>0$, $\Delta S_{\rm vN}=0$, which violates the Clausius inequality $\Delta Q\le T\Delta S_{\rm vN}$.

The work needed at time zero to rotate the spin is

$$W_0=-{\rm tr}\rho_G\frac{\varepsilon+\eta_a}{2}(\hat\sigma_x+\hat\sigma_z)=\frac{\varepsilon}{2}\tanh\frac{\beta\varepsilon}{2}+\frac{g\hbar\Gamma}{2\pi} \tag{28}$$

representing the work done on the spin and on the bath, respectively. It can be verified that the total work W_0+W_1 is always positive, so Thomson's formulation for a cyclic change [6] (here: the combination of the pulses at time $t=0$ and t) starting from equilibrium is obeyed.

Two pulses in a rotated initial Gibbsian state. If there are many spins, each in a slightly different external field, there appears an inhomogeneous broadening of the $\omega_0=\varepsilon/\hbar$ line, for which we assume the distribution

$$p(\omega_0)=\frac{2}{\pi}\frac{[\mathcal{T}_2^*]^{-1}}{(\omega_0-\bar\omega_0)^2+[\mathcal{T}_2^*]^{-2}} \tag{29}$$

having average $\bar\omega_0$ and inverse width $\mathcal{T}_2^*$, typically much smaller than $\mathcal{T}_2$. In this case the gain for a single pulse is washed out, leaving only the loss $\Delta Q=-g\hbar\Gamma/2\pi$, so two pulses are needed. We consider again the rotated initial Gibbsian state, and perform a first $-\frac{1}{2}\pi$ pulse around the x-axis at time t_1 and a second $\frac{1}{2}\pi$ pulse at time $t_2=t_1+\tau$. In the regime of small g and large $t_1\sim\mathcal{T}_2$ the work in the second pulse is

$$\begin{aligned}W_2&=\frac{g\hbar\Gamma}{2\pi}-\frac{1}{2}e^{-t_1/\mathcal{T}_2}\varepsilon\sin\omega_0\tau\;\tanh\frac{\beta\varepsilon}{2}\\&-\frac{1}{2}e^{-t_2/\mathcal{T}_2}\tanh\frac{\beta\varepsilon}{2}\;\cos\omega_0 t_1(\varepsilon\sin\omega_0\tau+gT\cos\omega_0\tau)\end{aligned} \tag{30}$$

At moderate times only slowly oscillating terms survive. They are the ones that involve $\Delta t=t_2-2t_1$. For the total work W_1+W_2 this brings

$$\begin{aligned}W&=\frac{g\hbar\Gamma}{\pi}-\frac{\hbar}{4}e^{-t_2/\mathcal{T}_2}e^{-|\Delta t|/\mathcal{T}_2^*}\tanh\frac{\beta\hbar\bar\omega_0}{2}\,\{\bar\omega_0\sin\bar\omega_0\Delta t\\&+[\frac{1}{\mathcal{T}_2}-\frac{{\rm sg}(\Delta t)}{\mathcal{T}_2^*}(1+\frac{\beta\hbar\bar\omega_0}{\sinh\beta\hbar\bar\omega_0})]\cos\bar\omega_0\Delta t\,\}\end{aligned} \tag{31}$$

For Δt near $2\pi n/\bar\omega_0$ such that the odd terms cancel, this again exhibits work extracted solely from the bath.

Bath-induced gain without inversion. It is common knowledge that a two-level system with population inversion, i.e. with a negative temperature, is capable to amplify light, and it represents the basic working mechanism of lasers and masers (see [10] for more non-standard mechanisms of lasing). In this context a bath is typically considered to be a drawback for the amplification, as being a source of undesirable noises and relaxation towards

equilibrium [10]. Our present aim is to show that the bath can nevertheless play a totally different role, namely in *assisting* work extraction (gain) by means of an *positive* temperature state in the two-level system. This effect is strictly prohibited by the second law applied to a positive temperature spin state if there were no coupling to the bath [6]. We consider separated initial conditions with $\langle\hat{\sigma}_x(t)\rangle = \langle\hat{\sigma}_y(t)\rangle = 0$, and apply a $-\frac{1}{2}\pi$ pulse at time $t_1 = 0^+$, and a $\frac{1}{2}\pi$ pulse at t_2. For $t_2 \gg 1/\Gamma$ the work is:

$$W = \Delta U - \Delta Q, \tag{32}$$

$$\Delta U = -\frac{\varepsilon}{2}[1 - e^{-\xi(t_2)}\cos\omega_0 t_2]\langle\hat{\sigma}_z\rangle + \frac{g\varepsilon}{4}e^{-\xi(t_2)}\sin\omega_0 t_2$$

$$\Delta Q = -\frac{g\hbar\Gamma}{\pi} + \frac{1}{2}gT\,e^{-\xi(t_2)}\sin\omega_0 t_2\langle\hat{\sigma}_z\rangle \tag{33}$$

where ξ was defined in (17). In the inversion-free case, the initial state of the spin is a Gibbsian connected to a positive temperature $T_0 = 1/\beta_0$, for which $\langle\hat{\sigma}_z\rangle = -\tanh\frac{1}{2}\beta_0\varepsilon \le 0$. Let us first investigate the case $T_0 = \infty$ (completely random state, $\langle\hat{\sigma}_{x,y,z}\rangle = 0$). The work W can be negative (gain) provided $\varepsilon > 4\hbar\Gamma/\pi$. This situation can be met in quantum optical two-level systems [10,11] and in NMR [12]. This mechanism concerns work extraction *with help of the bath* (it disappears for $g \to 0$), but *not from the bath*, since now $\Delta Q < 0$. The origin of the effect is that although the state of the spin was completely disordered initially, the first pulse does generate some coherence. Due to back-reaction of the bath one has after the pulses $\langle\hat{\sigma}_y(t_2)\rangle = \sin\gamma(t_2)\exp(-\xi(t_2))\sin\omega_0 t_2$, where $\gamma(t_2)$ of Eq. (9) goes from 0 to $\frac{1}{2}g$ on the timescale $1/\Gamma$, the reaction time of the bath.

At finite T_0 the term ΔU can still be negative when $T_0 \gtrsim \varepsilon/g$, which can be met for not-too-small g, a condition anyhow needed for having a sizeable effect. ¿From a thermodynamic point of view the gain can be seen as a flow of energy from a high temperature (of the spin) to a lower one (of the bath), and the outside world (gain).

Feasibility. Let us present several reasons favoring the feasibility of the proposed setups: 1) Two-level systems are widespread, not the least because many quantum system act as two-level under proper conditions; 2) Detection in these systems is relatively easy, since already one-time quantities $\langle\vec{\sigma}(t)\rangle$ completely determine the state; 3) The harmonic oscillator bath is universal [13]; 4) Work and heat were measured in NMR experiments more than 35 years ago [14]; 5) Our main effects do survive the averaging over disordered ensembles of spins, thus allowing many-spin measurements. 6) The ongoing activity for implementation of quantum computers provides experimentally realized examples of two-level systems, which have sufficiently long $\mathcal{T}_2$ times, and admit external variations on times smaller than $\mathcal{T}_2$: (*i*) for atoms in optical traps $\mathcal{T}_2 \sim 1$s, $1/\Gamma \sim 10^{-8}$s, and there are efficient methods for creating non-equilibrium initial states and manipulating atoms by external laser pulses [11]; (*ii*) for an electronic spin injected or optically excited in a semiconductor $\mathcal{T}_2 \sim 1\,\mu$s [15]; (*iii*) for an exciton created in a quantum dot $\mathcal{T}_2 \sim 10^{-9}$s [16] (in cases (*ii*) and (*iii*) $1/\Gamma \sim 10^{-13}$s and femtosecond (10^{-15}s) laser pulses are available); (*iv*) in NMR physics $\mathcal{T}_2 \sim 1 - 10$s and the duration of pulses can be comparable with $1/\Gamma \sim 1\,\mu$s.

Conclusion. Like in the oscillator model [4], the Clausius inequality can be violated in the spin-boson model, namely by a single pulse. For many spins this typically does not happen in the first pulse; it may occur in the second pulse, while it is absent for the two pulses taken together, because of intermediate entropy increase. Work can be extracted from the equilibrated bath, for the single spin case by one pulse, and for the many spin case by two pulses. This contradicts Thomson's formulation of the second law: no gain from cycles. Gain is also possible from a positive temperature (inversion-free) initial state, which may serve as a principle for bath generated lasing and masing. These effects are not in a conflict with the *equilibrium* Thomson formulation of the second law, and are fully quantum: they disappear at high temperatures and they do not occur for classical pulses.

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